Title

MICROANALYSIS OF POLYTYPOID CERAMICS BY IMAGING, DIFFRACTION AND SPECTROSCOPY

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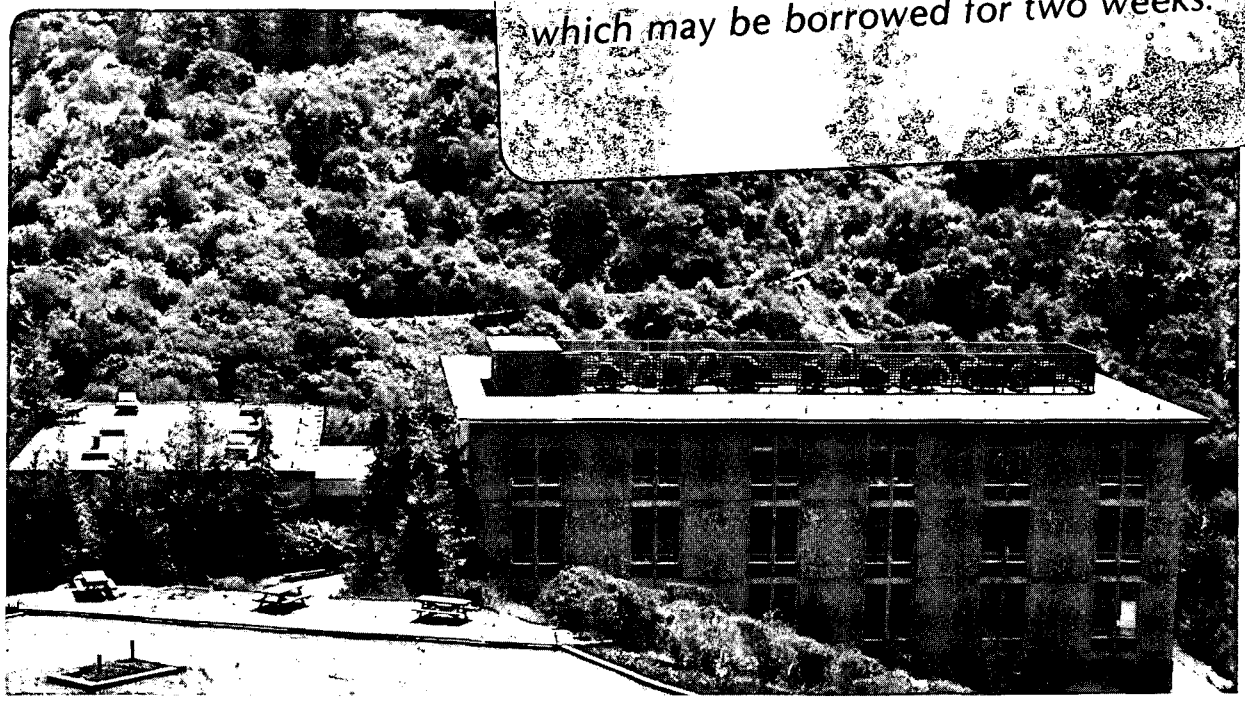

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DISCLAIMER

MICROANALYSIS OF POLYTYPOID CERAMICS BY IMAGING, DIFFRACTION AND SPECTROSCOPY

K.M. Krishnan and G. Thomas

Combined atomic resolution imaging, microdiffraction and energy dispersive X-ray microanalysis suggest that the 32H polytypoid in the AlN-Al_2O_3 pseudobinary system is in fact a 7:9 periodic intergrowth of the 21R and 27R polytypoids. Furthermore, these combined techniques verify that the cation/anion ratio is 16/17 and that this ratio defines the polytypoid precisely.

Introduction

The processing of structural ceramics generally involves additions which either modify the structures, their interfaces, or both. Well-known examples are oxide additives to sintered or hot-pressed Si_3N_4 which produces intergranular glassy and/or crystalline phases. The avoidance of glassy phases is necessary for optimum refractory performance[1]. On the other hand, it has been shown that a variety of compositions in the Al_2O_3-AlN pseudobinary system can be successfully processed to almost theoretical densities without the use of additives[2]. In addition to the fact that the

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end members of the above composition-tieline are, independently, potential candidates for advanced structural applications, the system is of fundamental importance because the various microstructures are largely anion controlled[3]. However, at either end of the phase diagram, small additions of the other end member results in a variety of modulated structures based on the wurtzite (AlN rich end) structure[4] and having anisotropic grain shapes elongated parallel to the {0001} fault plane in the above structure ($P6_3mc$).

An assortment of modulated structures at the AlN rich end of the Al_2O_3-AlN phase diagram, called compositional polytypes or polytypoids, including SiO_2 sintered AlN [5] have been reported[4-7]. It has been argued that the structures of all these polytypoids are strictly determined by their composition and a specific cation/anion ratio can be associated with each structure. However, the compositions identified with a particular structure are contradictory[4,8] and the experimental confirmations are often incomplete[7].

Recent studies of the AlN-Al_2O_3 system produced by reaction sintering resolved a new polytype designated 32H [6]. This paper reports a further study by high resolution imaging, microdiffraction, and energy-dispersive X-ray spectroscopy in order to understand this system and to probe directly whether the predicted cation/anion ratio of 16/17 for the 32H structure--which assumes ideal charge balance in the absence of point defects--is in fact valid.

Experimental Procedure

Samples of a nominal starting composition of 95 mol% AlN (rest Al_2O_3) and an actual composition of 85 mol% AlN were prepared by a reaction sintering process[2]. The starting powders were ball-milled using an ethanol fluid medium for 24 hours, isostatically pressed at 25,000 psi and prereacted at

1200°C for 24 hours in gas-tight flowing nitrogen before final sintering. Final reaction sintering was then carried out at temperatures of 1950°C-2100°C for one hour in an inductively-heated graphite furnace with flowing nitrogen.

TEM specimens were prepared by cutting thin slices of the ceramic with a diamond saw, grinding and polishing to form 40μm thick slices and finally ion-milling to perforation using Argon ions accelerated through a potential of 5 kV. The specimens were coated with a thin layer of evaporated carbon to avoid surface charging. They were then examined in a JEOL 200CX TEM operating at 200kV by conventional SAD, CBED and phase contrast imaging techniques. Optical microdiffraction was carried out from small regions of the photographic negative using a He-Ne laser. The microanalysis was carried out on another dedicated JEOL 200CX analytical electron microscope fitted with an ultra thin window detector (resolution - FWHM ~ 109 eV for F $K\alpha$ X-rays). EELS was also studied but the X-ray data proved to be superior. The K-factors required for the microanalysis were all determined experimentally[9]. Finally, structure images were obtained using the JEM Atomic Resolution Microscope operating at 1000kV, with a demonstrated point-to-point resolution of 0.16 nm.

Results and Discussion

Figures 1a, b, c show a selected area diffraction pattern, conventional lattice image and an optical diffractogram from a region of the sample of a "32H" polytypoid structure. The position of the 010 spot with respect to the transmitted beam in the SAD (Fig. 1a), confirms the hexagonal stacking sequence. From the diffraction pattern, the repeat distance along the c-axis can be calculated to be 8.3nm for this polytypoid. However, the lattice image (Fig. 1b) and the accompanying optical diffractogram (Fig. 1c) both show a

spacing of 4.3nm. This is not surprising, for the nH polytypoids in this system normally consist of two blocks of n/2 layers related by a c-glide plane[4]. This is verified in Figure 2 which shows a CBD pattern oriented such that the c-axis is parallel to the incident beam. Using the radius of the FOLZ ring, G_1 the periodicity along the c-axis is calculated to be 4.2nm, which confirms the above structural predictions. However, this CBD pattern was obtained using a 60nm diameter probe and hence the information obtained is averaged over a much larger area than that of a unit of the 32H structure. When direct imaging using atomic resolution is used, as shown in Figure 3, a periodicity is resolved which can be sequenced as alternate [7:9:7:9] repeats. This can be interpreted as parallel intergrowths of the 27R (c = 7.2nm) and 21R (c = 5.7nm) polytypoids. Clearly adjacent units of 27R plus 21R add up to the "32H" repeat unit. A detailed interpretation of these images would require simulations for a predicted structure of the unit cell. Image calculations, using the multislice method[10], are currently in progress. Similar intergrowths have also been observed in the SiC polytype structures[10].

In order to analyze this further it is necessary to measure the cation/anion ratio. A typical EDS spectrum obtained from a "32H" region of the sample, is shown in Fig. 4. The analysis carried out using carefully determined experimental K-factors[9] suggest a composition of 47.9 at % Al, 13.8 at % O and 38.3 at % N. Within experimental error ($\pm$3 % in the microanalysis) the anion/cation ratio measured (1.08) is in agreement with the theoretically predicted ratio (17/16 = 1.06). Unlike previous erroneous attempts[7] using a combination of EELS (with approximately 30 % error in analysis) for the study of anions and EDXS for the study of the cations, this evidence conclusively supports the view that the ratio defines the polytypoid. In addition, direct atomic resolution imaging indicates that the structure is not a new 32H phase but periodic 7:9 intergrowths of 21R and 27R.

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Figure Captions

Figure 1: (a) SAD pattern of the "32H" polytypoid structure taken such that the c-axis is perpendicular to the incident beam. The reflections corresponding to the 00.32 reflection indicate that c = 8.3nm.

(b,c) Lattice image and the corresponding optical diffractogram from the same region of the specimen. 4.3nm fringes corresponding to half the unit cell reveal the presence of a c-glide plane.

Figure 2: CBED pattern taken with the incident beam parallel to the c-axis. The diameter of the FOLZ ring confirms a c-repeat of 4.24nm.

Figure 3: Typical EDX spectra acquired with a KEVEX UTW detector. The accompanying microanalysis using experimentally determined K-factors confirms the cation/anion ratio of 16/17.

Figure 4: Atomic resoluion image of the 32H polytypoid at 1000kV. Note that the 32H structure is actually due to a parallel intergrowth of the 21R and 27R polytypoid structures.

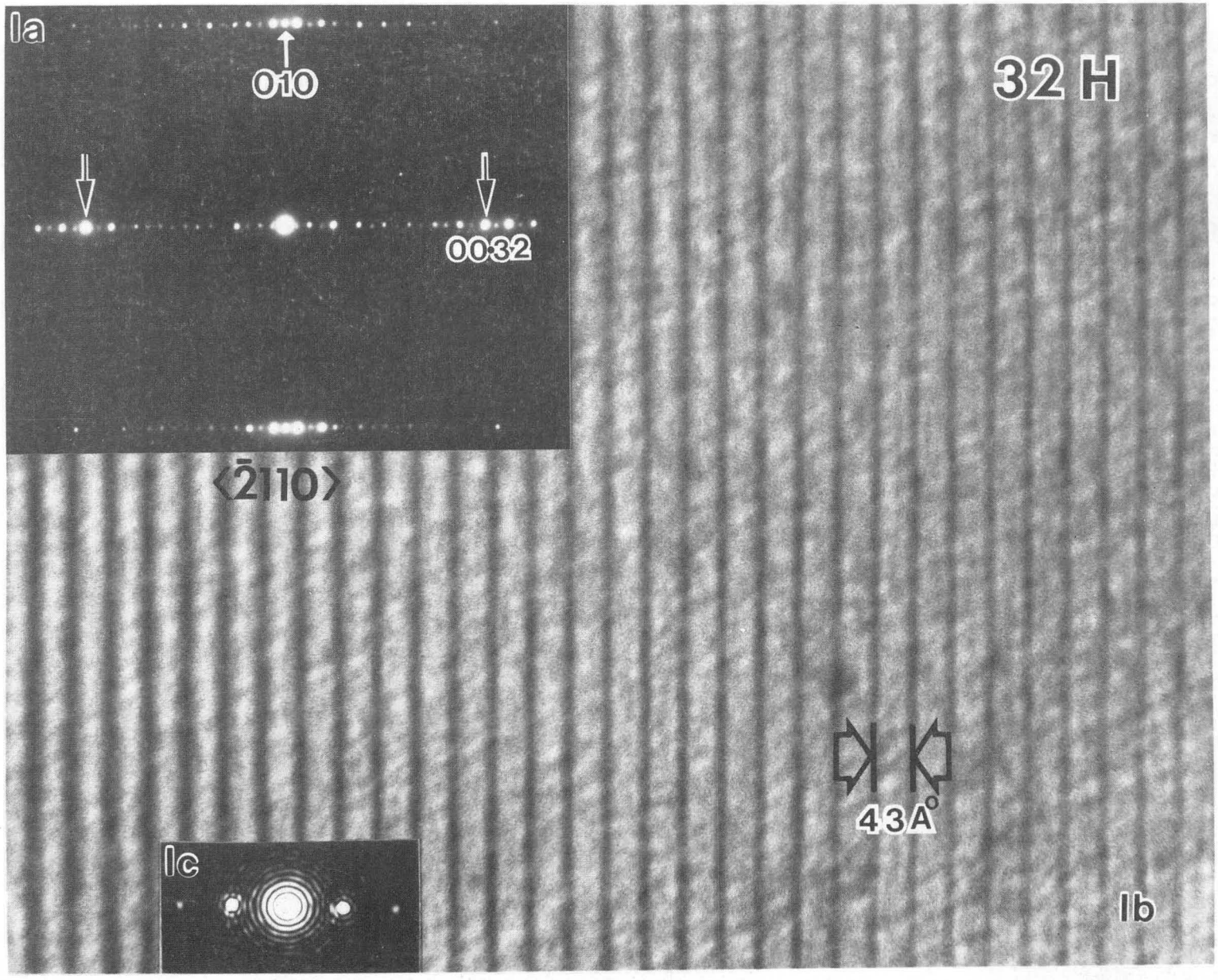

Fig. 1

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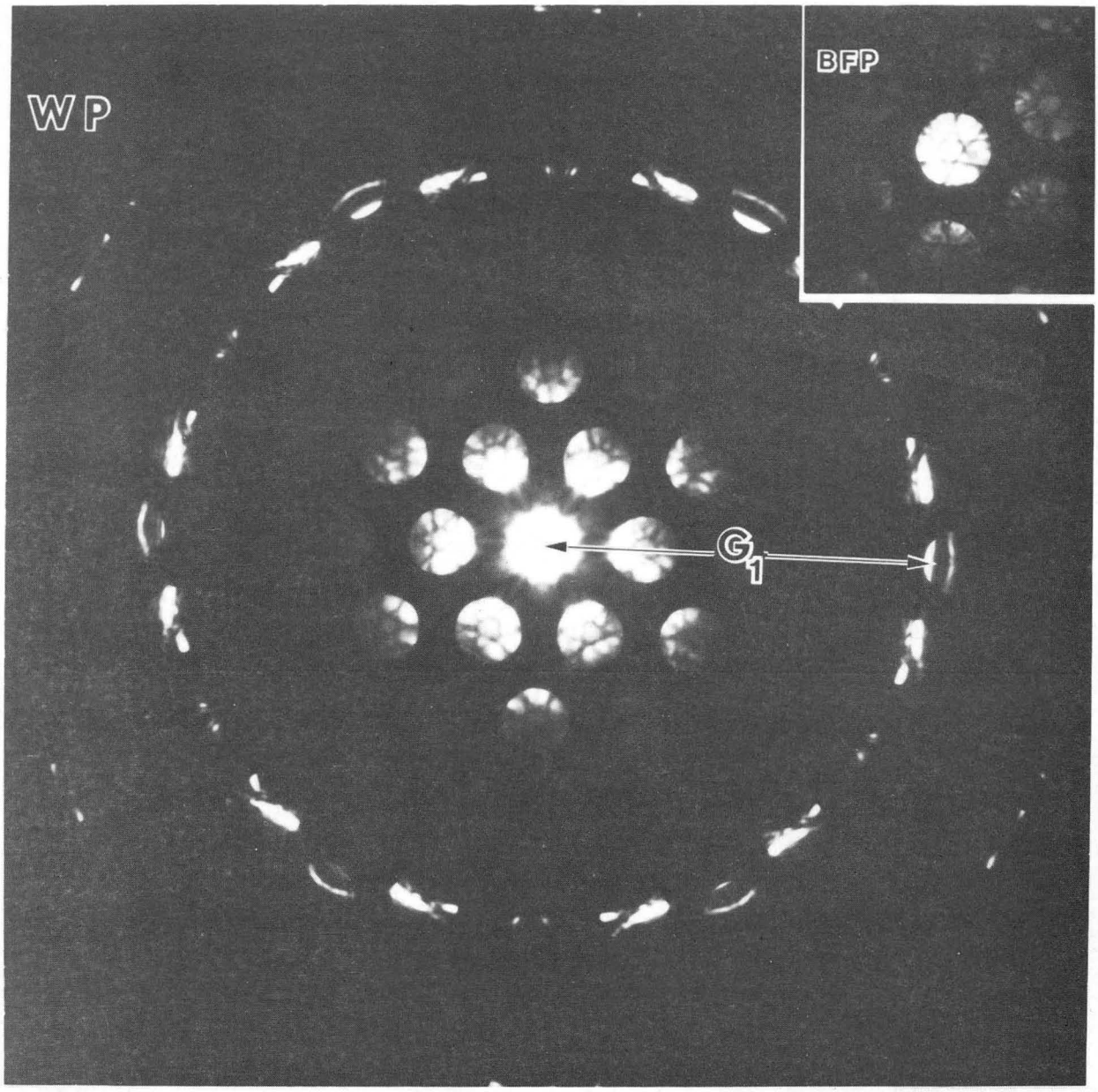

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Fig. 2

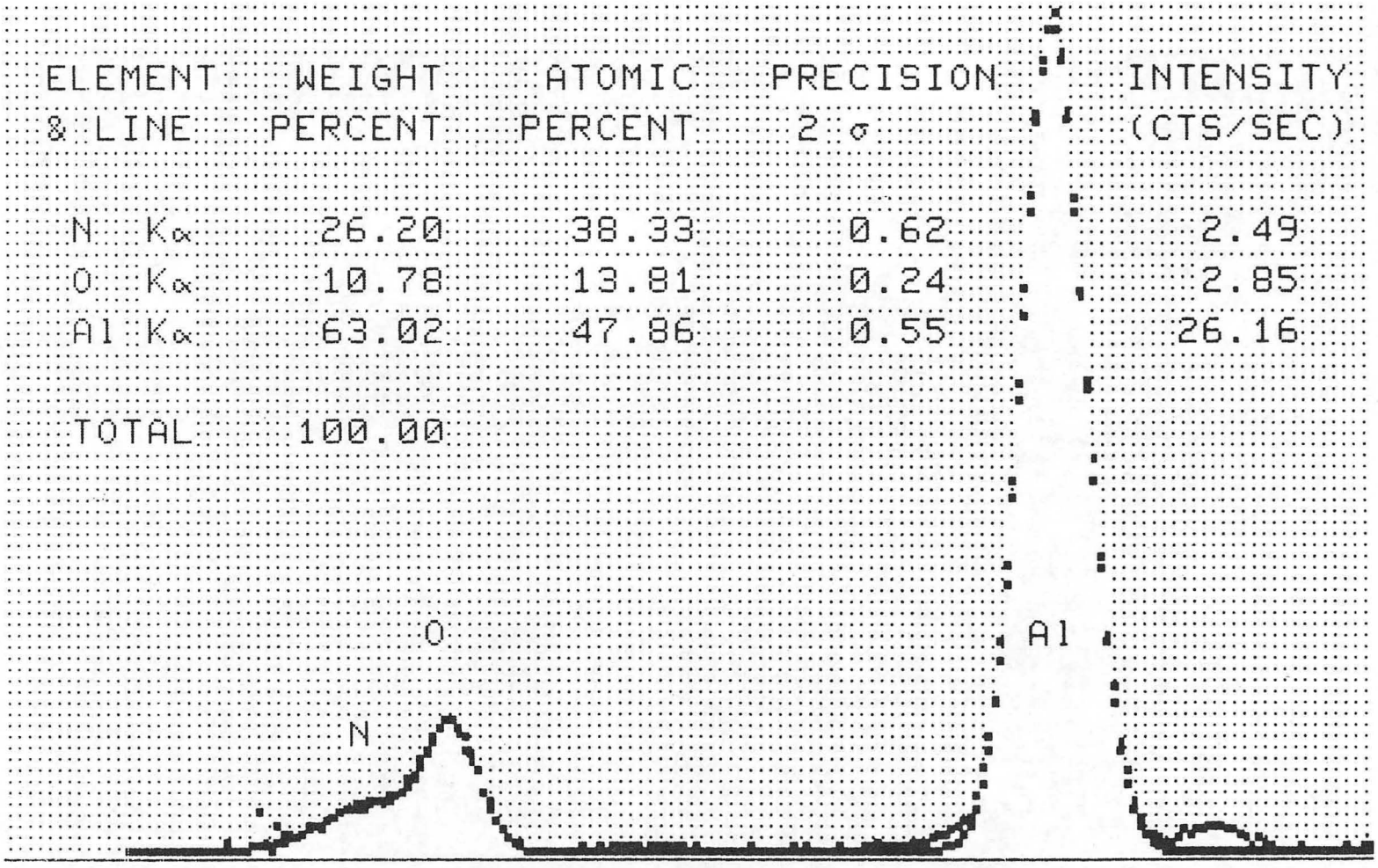

Fig. 3

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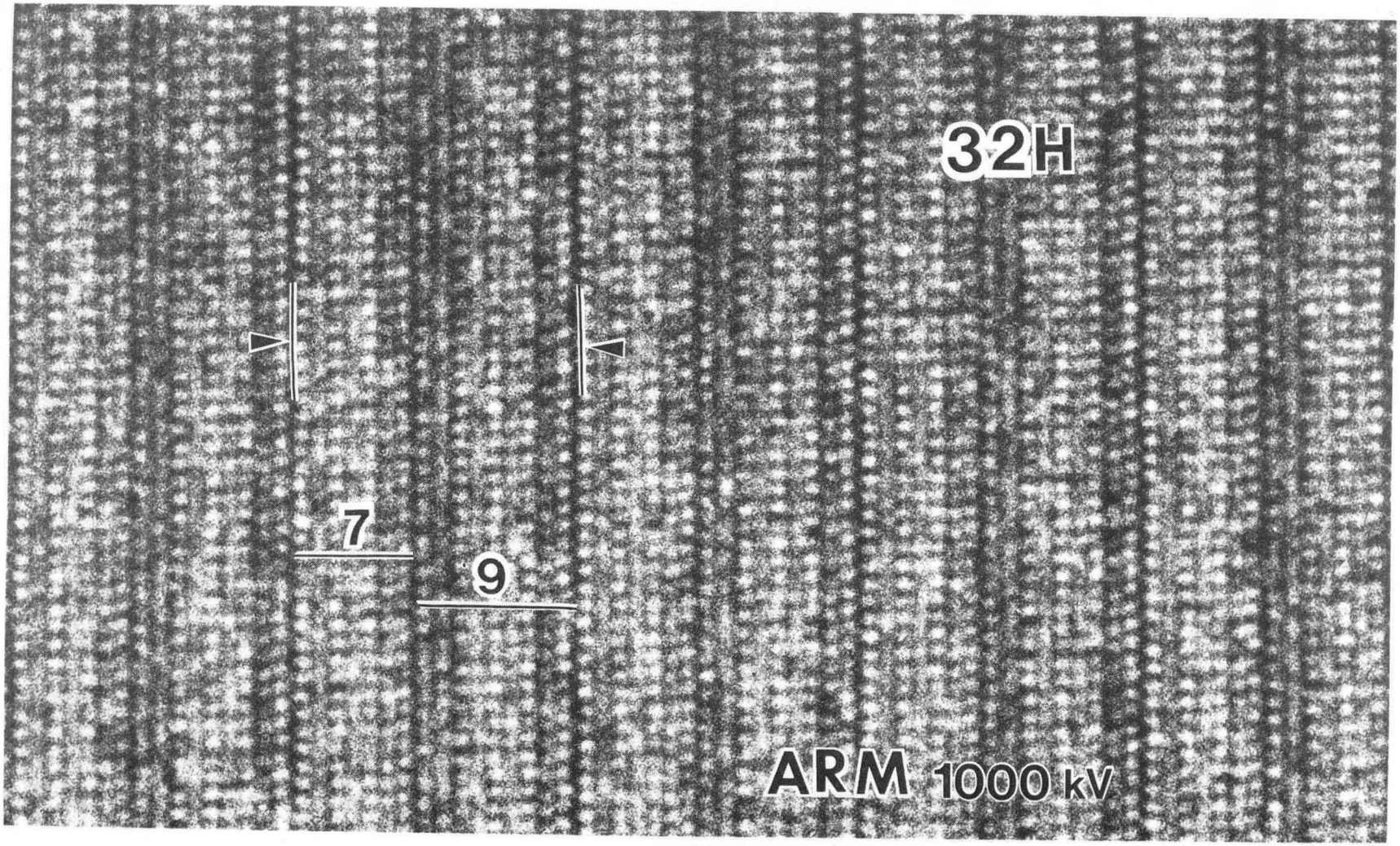

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Fig. 4

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